PROBLEMS IN THE ELECTROLYTIC PREPARATION OF PERCHLORIC ACID FROM SODIUM CHLORIDE

BY

ARNOLD JOHN VERAGUTH

A.B., Wabash College, 1937

M.S., Purdue University, 1939

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1943

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Introduction

The manufacture of perchloric acid from sodium chloride involves the following steps: 1. the electrolytic oxidation of sodium chloride to the chlorate[1]; 2. a second electrolytic oxidation of sodium chlorate to the perchlorate; 3. the treatment of pure sodium perchlorate by metathesis with concentrated hydrochloric acid which almost quantitatively precipitates sodium chloride[2]; and 4. the subsequent isolation of perchloric acid by concentration of the filtrate to evolve the hydrochloric acid[2]. An alternative scheme involves the formation of ammonium perchlorate from the sodium perchlorate followed by the oxidation of its ammonia content by mixed nitric and hydrochloric acids[3]. A second alternative is the electrolytic oxidation of hydrochloric acid by the Goodwin and Walker[4] process which has never been used as the basis for the industrial operation in quantity production.

The elimination of the foreign supply sources of sodium or ammonium perchlorate due to the present world war has resulted in the construction of numerous manufacturing units in the large scale production of perchloric acid from sodium perchlorate. The construction and operation of the cell employed in the electrolytic oxidation of sodium chlorate to perchlorate for quantity production has not been previously described. The present equipment so far as is known involves the exclusive use of platinum anodes and iron cathodes. The electrolytic cell does not employ a partition to separate anolyte from catholyte. As a result, near the end of the reaction the current efficiency falls off and the wasted energy results in the production at the anode of ozone and oxygen. This gaseous mixture from the anode is free to mix with the hydrogen from the cathode reaction and the consequence is the formation of an explosive gas mixture. Hence, in the operation of the cell, at the completion of each oxidation, which must be carried out to the complete removal of all chlorate up to 99.5% minimum oxidation, care must be taken to prevent ignition of the gas mixture of the cell or disastrous explosions may be encountered. The use of sodium perchlorate of greater than 0.5% sodium chlorate content similarly would cause explosion when the hydrochloric acid metathesis to form perchloric acid is carried out.

The remedy to this situation involves the completion of the sodium chlorate oxidation to 95% followed by the removal of the chlorate impurity by electrolytic reduction which can not result in any reduction of perchlorate but does eliminate explosion hazards both in the cell oxidation and sodium perchlorate metathesis following for the production of perchloric acid.

A study was, therefore, made of the proper cell design for use in the oxidation of sodium chlorate to perchlorate, the performance of such a cell under working conditions, and the development of an analytical procedure for the determination of chlorate in the presence of perchlorate. The proper selection of electrodes and cell design for the electrolytic reduction of chlorate to chloride in the presence of sodium perchlorate was also studied.

PART I

The Quantitative Determination of Chlorates in the Presence of Perchlorates

The object of the present section was to develop an accurate and convenient method of chlorate analysis which could be applied to check the sodium chlorate content in an electrolytic cell liquor used to prepare sodium perchlorate from sodium chlorate. The method, therefore, had to be applicable in the presence of perchlorates.

The oxidation potential of chloric acid with respect to its reduction to chloride is + 1.45 volts as given by Latimer[5], and from thermodynamic considerations chloric acid should be a strong oxidizing agent. In reality the kinetics of its reactions are such that its reduction is extremely sluggish. This situation is very apparent from the fact that its electrolytic preparation starting with hydrochloric acid is successful without the use of a diaphragm cell[4]. From general considerations the reducing agents with the best possibilities for use are ferrous sulfate and sodium arsenite. Gleu[6] employed sodium arsenite in excess to reduce chlorates to chlorides in the presence of osmic acid. Since the data, given by Gleu, are of limited scope, it was deemed advisable to thoroughly study this convenient reaction. Ferrous sulfate as reductant was similarly used to reduce chlorates in the presence of sulfuric acid with osmic acid as catalyst.

Sodium and potassium chlorate salts recrystallized from water and dried at 90° C. were established as standard of reference purity salts by the following procedure: One hundred and fifty

milligram samples are dissolved in water, and 0.15 ml. of 0.01 M OsO_4 in 0.1 N H_2SO_4 is employed as catalyst. An excess of approximately 0.25 N sodium arsenite is added along with sufficient 9 M H_2SO_4 to make the reaction mixture 1 N in acid concentration. A reaction time of at least fifteen minutes is allowed after which the excess reductant is back-titrated with standard 0.1 N sulfato ceric acid in 1 M H_2SO_4 using ferroin as indicator. In this procedure it was not necessary to add sodium bicarbonate to the reaction mixture to exclude air as was pointed out by Gleu[6].

The presence of perchloric acid instead of sulfuric acid in the above procedure offers no interference in the chlorate determination.

The procedure for ferrous sulfate as reductant is similar to that given for the sodium arsenite except that the reaction time necessary is longer, namely, thirty minutes are required at the 1 N sulfuric acid concentration; when the acid concentration is 3 N H_2SO_4, the reaction time is shortened to fifteen minutes.

PART II

The Electrolytic Reduction of Sodium Chlorate

The problem at hand was to select a metal cathode which would reduce the residual 5% of sodium chlorate in the commercial electrolytic cell which produces sodium perchlorate from the chlorate.

F. Foerster[7] and E. Müller[8] studied the relationships occurring from the electrolytic reduction of neutral alkali chlorate solutions by various metals. They asserted that a strong reduction was observed by iron and a weak reduction by cobalt, but that the reduction by a whole series of other metals was completely absent. McLaren, Davis, Pitmann, and Groggins[1] who have perfected the conditions for the commercial electrolytic production of sodium chlorate from sodium chloride have published information to prevent the reduction of chlorate. They emphasized that rusty iron cathodes effected reduction at the cathode to the extent of 100%, but a clean iron surface gave only a small amount of reduction. In acid solutions with cathodes of zinc, cadmium and platinum Voege[9] found electrolytic reduction occurred, but to work with acid solutions in the practical problem as stated is undesirable.

In this study only neutral media were considered. The metals employed as cathodes were platinum, nickel, tin, tungsten, molybdenum, chromium, bismuth, carbon, zinc, and iron, all of which gave negative results except iron.

The apparatus used to study the mentioned metal cathodes was described. The use of a diaphragm cell was found to be unessential. Subsequent operations were in a cell without a diaphragm and the platinum anode area was reduced from 400 to approximately 10 sq. cm.; the iron cathode area was 100 sq. cm. With these conditions the reduction of the 5% sodium chlorate solutions varied from 45 to 58% at current densities from 0.01-0.04 amps. per sq. cm. of cathode area. A synthetic cell liquor prepared with 76 gm. $NaClO_4$ and 4 gm. $NaClO_3$ per 100 ml. showed reductions of 99.0, 99.6, 99.4, and 99.9 at the respective current densities of 0.01, 0.02, 0.03 and 0.04 amps. per sq. cm. On the basis of this data, therefore, it would seem practical to employ this information in the actual operation of a perchlorate cell to eliminate the explosion hazard near the end of the complete oxidation of sodium chlorate to the perchlorate. Thus, a 95% oxidized perchlorate cell liquor could be freed of its residual 5% chlorate content by electrolytic reduction using a large area iron cathode and a platinum anode of small area at a current density of 0.02 or 0.03 amps. per sq. cm. at the cathode.

Since the presence of chromates retards the reduction at the iron cathode, it is proposed to use either of the metals studied to reduce chlorates, which gave negative results, in the absence of chromates. Then, assuming that identical hazards are involved near the end of the completed oxidation, the cell liquor could be transferred to a cell with an active rusty iron cathode to free the cell liquor from its chlorate content. The perchlorate ion will not reduce, and the presence of chloride does not interfere with the subsequent operation to obtain perchloric acid from the sodium perchlorate.

PART III

Description and Operation of a Commercial Cell for the Electrolytic Oxidation of Sodium Chlorate to Sodium Perchlorate

Little practical information is in the literature concerning a suitable cell design and operation characteristics for quantity production of sodium perchlorate from the chlorate. The cell

construction is described consisting of a glass lined steel tank 2.875′ by 2.815′ in cross section by 5.5′ in length. Eight electrode assemblies are mounted in the tank on each of the two side walls. Each electrode assembly consists of a 2.5″ diameter iron pipe 27″ long as cathode which supports a coaxial platinum clad copper rod anode by means of porcelain insulators. The steel tank serves as the contact to the bus bar cathode which leads to the source of power. Multiple bus bar contacts to the anodes complete the circuit. The capacity of the described perchlorate cell is approximately 250 gallons, and a saturated solution of sodium chlorate along with 4 pounds of potassium dichromate which is added to inhibit the sodium chlorate reduction are introduced as the cell liquor. Data are given for the cell operation at a current density varying from 320 to 492 amps. per sq. ft. of anode surface at a voltage range from 5.8-6.5 volts across each electrode assembly. The current efficiency of the operation is around 53%. It is apparent from the data obtained that the oxidation does not proceed smoothly until the electrodes are sufficiently activated. A smooth oxidation continues after 24 hours until 65% oxidation is reached, at which point a great deal of current is consumed to liberate oxygen and ozone at the anode. The electrolytic reduction of the remaining chlorate as proposed in Part II is recommended to eliminate the obvious hazard, when the cell liquor is 95% oxidized.

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VITA

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